



Properties and Performance Attributes of Novel Co-extruded Polyolefin Battery Separator Materials

Part 1: Mechanical Properties

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Abstract

As NASA prepares for its next era of manned spaceflight missions, advanced energy storage technologies are being developed and evaluated to address future mission needs and technical requirements and to provide new mission-enabling technologies. Cell-level components for advanced lithium-ion batteries possessing higher energy, more reliable performance and enhanced, inherent safety characteristics are actively under development within the NASA infrastructure. A key component for safe and reliable cell performance is the cell separator, which separates the two energetic electrodes and functions to prevent the occurrence of an internal short-circuit while enabling ionic transport. Recently, a new generation of co-extruded separator films has been developed by ExxonMobil Chemical and introduced into their battery separator product portfolio. Several grades of this new separator material have been evaluated with respect to dynamic mechanical properties and safety-related performance attributes. This paper presents the results of these evaluations in comparison to a current state-of-the-practice separator material. The results are discussed with respect to potential opportunities to enhance the inherent safety characteristics and reliability of future, advanced lithium-ion cell chemistries.

Introduction

As NASA embarks on a renewed human presence in space, human-rated electrical energy storage and power generation technologies that demonstrate reliable performance in a variety of unique mission environments will be required. To address the future performance and safety requirements for the energy storage technologies that will enhance and enable future aerospace missions, advanced rechargeable lithium-ion battery technology development has been pursued within the NASA Exploration Technology Development Program's (ETDP) Energy Storage Project, with an emphasis on addressing performance technology gaps between state-of-the-art capabilities and critical future mission requirements.

Recently, lithium-ion batteries have been qualified to provide electrical power needs for life support hardware associated with manned extravehicular activities in space. Currently, both cell and cell component development efforts are focused on improving the overall safety, as well as the electrochemical attributes, of such battery systems in order to optimize their performance for manned space applications. A key cell component of a lithium-ion battery which significantly impacts both of these performance features is the battery separator.

Battery Separator Properties and Characteristics for Rechargeable Lithium-based Cells

The function and reliability of the separator is critical for the optimal performance and safety of a lithium-ion cell. In nonaqueous, liquid-electrolyte cells that exemplify a lithium-ion cell chemistry, the separator is typically a non-electrically-conducting porous electrolyte-filled media or membrane, which is sandwiched between and in contact with the two active, solid electrodes. Its roles are to prevent direct electronic contact between the two electrodes, which would result in a short-circuit, and to allow the flow of ionic species within the cell. Certain separator materials can also function as internal cell safety devices. The separator affects the internal cell resistance, stability, cycle-life, operating temperature range and cell kinetic parameters such as discharge and charge rates. By its ability to regulate the electrolyte distribution between the active electrodes, as a result of its morphology and permeability characteristics, the separator limits ionic diffusion and recombination rates, and, thus, impacts cell capacity, power and available energy. With respect to the inherent safety of a lithium-ion cell, the separator may afford passive protection and tolerance to cell abuse conditions that may arise, and it can enhance the overall cell safety by providing another level of internal redundancy (i.e., complement cell designs that incorporate safety devices such as a positive temperature coefficient (PTC) resistor and/or a current interrupt device (CID)).

The structural and physiochemical properties of the separator material strongly influence the overall cell performance, although the separator does not “actively” participate in the battery operation. The mere presence of the separator component within a cell adversely affects both electrical and mass-related performance, as it adds electronic resistance and occupies limited space. For electrochemical cell chemistries in which the liquid electrolyte solution serves only as an ionic conductor, the separator should be as thin as possible and porous, but yet possess the required physical strength to maintain the mechanical and electrical separation between the solid electrodes. These characteristics are essential in order to achieve high energy and power densities for applications requiring such performance attributes. Thus, the practical design of a separator is an art, as there is a compromise between the degree of porosity of the material and its mechanical strength. For battery safety, a battery separator for utilization with lithium-based cell chemistries should have the inherent ability to shut the battery down if overheating occurs. Several comprehensive reviews of battery separators in general (Refs. 1 and 2) have appeared in the literature, as well as some with a primary emphasis on lithium-based cell technologies (Refs. 3 to 5). Recently, a NASA applications-focused summary review was prepared which elucidated primary separator properties and characteristics for rechargeable lithium-based cells, how the separator properties influence cell performance and safety and how degradation of the separator component may result in overall cell failure (Ref. 6).

In summary, the overall *mechanical strength* of the separator is characterized in terms of several factors, each possessing desired requirements and performance metrics. *Tensile strength* and related properties are strongly dependent upon the material manufacturing process. Uniaxially-oriented separator films are generally preferred for material *dimensional stability*, as they exhibit a minimal tendency to shrink at elevated temperatures or when exposed to electrolyte. High *puncture strength* is important to prevent the penetration of particulate electrode material through the separator, especially during cell assembly, which could lead to an electrical short circuit. High mechanical strength is important, especially in a uniaxially-oriented separator film’s machine direction, as the material is subjected to considerable tension in this direction during the winding operation of a spiral-wound battery fabrication procedure, and contraction of the width during the operation would be undesirable. Biaxially-oriented films are more uniformly strong in both the machine and transverse directions.

State-of-the-Art Microporous Polymeric Membranes

Presently, most commercially-available lithium-ion spiral-wound cylindrical and prismatic cells and flat-plate cells containing a liquid organic electrolyte employ a microporous polymeric membrane separator due to advantages of performance, safety, and cost. These separators are based on polyolefin

materials, such as polyethylene (PE), polypropylene (PP) and blends of such. Such polyolefin-based separators, which afford both excellent chemical stability and mechanical properties, are manufactured by either a wet or a dry process, both of which employ orientation steps to introduce porosity and increase tensile strength. The wet process, or phase inversion process, involves mixing a polyolefin resin with a hydrocarbon liquid or low molecular weight oil, melting the mixture, extruding the melt into a sheet, orientating the sheet and extracting the liquid phase. An advantage of the wet process is that separator films can be created which exhibit uniform microporous fibril structures and uniform physical properties, which can provide stable battery performance and reliable safety. Polyolefin battery separators made by the wet process are available from several sources, such as a widely used polyethylene-based material from ExxonMobil Chemical and its Japanese affiliate Tonen Chemical.

For practical lithium-ion cell performance most microporous separators have a thickness well below 50 μm and average pore diameters below 1 μm . For high energy density applications, separator thicknesses of <25 μm are desirable in order to achieve a lower internal resistance and higher rate capability, however, the safety concern with respect to mechanical integrity and penetration must be considered. The tortuous and interconnected porous structure of a wet-process made material is more suitable for a cell with a long cycle life requirement. This is because the resulting microstructure from the wet-process aids in suppressing the growth of dendritic lithium metal on the anode surface during fast or low-temperature charging (Ref. 4). Desired values of key mechanical properties of separators for conventional lithium-ion cell chemistries are shown in Table 1.

TABLE 1.—KEY SAFETY-RELATED MECHANICAL PROPERTIES OF LITHIUM-ION CELL SEPARATOR MATERIALS (REF. 2).

Cell Safety-related Separator Characteristics

- Low dimensional shrinkage (<5 percent)
- High puncture strength (>300 g/mil)
- Tensile strength (>1000 kg/cm²)
- Elevated-temperature melt integrity (>150 °C)

Co-extruded ExxonMobil Battery Separator Grades

In the 2006-07 timeframe, the introduction of novel co-extruded battery separator grades by ExxonMobil Chemical created new opportunities in lithium-ion battery technology innovation and performance improvements. Based upon wet, bi-orientation process technology, the co-extruded polyolefin grades afford a new flexibility and versatility to the company's commercial battery separator product portfolio, which had a heritage of mono-layer grades based upon polymer membrane technology attributed to their affiliate, Tonen Chemical. Tonen, which is based in Japan, had supplied the microporous film for the first lithium-ion battery introduced in 1991 by Sony.

The ExxonMobil co-extruded multi-layer separator materials, which are based on tailored, heat-resistant polymer formulations, feature significant improvements in both porosity, which leads to lower internal cell resistance, and thermal properties compared to their predecessors (Ref. 7). Improved thermal meltdown properties can extend the mechanical integrity of the separator film for a longer time during a thermal event, giving the cell more time to dissipate the generated heat, thus, decreasing the probability of a more catastrophic event.

The co-extrusion process for polymeric film formation is based upon bringing selected thermoplastic polymers simultaneously together in an extrusion die, and they subsequently exit from the die in a planar form as a multi-layer structure. Each layer is formed by a separate polymer feed stream into the extrusion die, and the discrete layers are bonded together at their interface by a commingling of the polymers. Generally, the feed streams are of dissimilar polymers with respect to their chemical nature (e.g., polyethylene (PE) and polypropylene (PP)) and/or polymers of similar chemical nature but having

dissimilar properties (e.g., molecular weight, rheology, density, additives, etc.). Additives to the polymers can modify or enhance the performance or properties of an individual layer or the overall separator, and such modifications may include:

- (1) Lowering the melting temperature of the polymer.
- (2) Improving the melt integrity of the film (e.g., adding inorganic fillers, fine fibers, high melting point organic materials, etc.)
- (3) Improving the separator strength (e.g., adding elastomers, fine fibers, etc.)
- (4) Improving the separator surface wettability (e.g., adding wetting agents)
- (5) Improving the polymer processing (e.g., adding waxes, fluoropolymers, etc.)
- (6) Improving the separator flame retardant nature (e.g., adding phosphate esters, etc.)

After extrusion of a multi-layered, nonporous precursor separator, the precursor is processed (e.g., by a wet process) to form the micropores of desired porosity and tortuosity.

The *shutdown* property of a polymeric separator material can internally provide a margin of safety against an external short-circuit, accidental overcharge or an abuse condition resulting in an elevated cell temperature. A shutdown separator closes off its micropores when an internal temperature threshold (e.g., 130 °C) is exceeded, essentially shutting down the activity (e.g., the flow of ions) of the battery. In a scenario where the internal temperature is rising rapidly, however, the separator film can melt, thereby eliminating the physical barrier. Per company literature, the ExxonMobil Chemical/Tonen-developed film can retain the original shutdown temperature of the polyolefin material and, additionally, retain its mechanical integrity for an additional 40 °C. By not melting until a higher temperature is reached, the new separator film provides more time for the malfunctioning cell to dissipate its heat, reducing the potential for transferring the heat to its neighbors and setting off a larger thermal event (Ref. 9). Enhanced thermal mechanical properties of the co-extruded grades are illustrated in Figure 1, which is representative strain versus temperature data from ExxonMobil's product literature. As illustrated in the figure, a larger temperature differential (i.e., safety enhancement) between the shutdown and meltdown temperatures is evident for the co-extruded material, although the two materials have similar visual appearances as the temperature is increased.

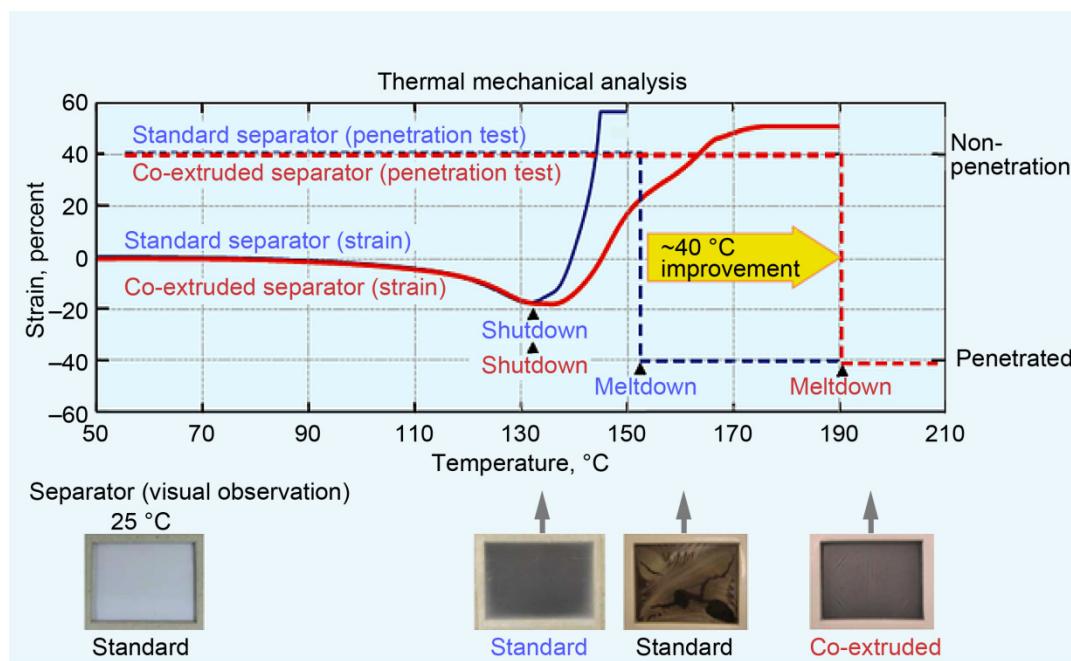


Figure 1.—Thermal mechanical properties of ExxonMobil/Tonen battery separator products (Ref. 9).

Experimental

Samples of the co-extruded polyolefin battery separator films under investigation in this report were obtained from the ExxonMobil Chemical Company, Macedon, New York. Experimental laboratory assessment results for the key mechanical properties for four grades of co-extruded films, which are identified by ExxonMobil as V25EKD, V25CGD, V20EHD, and V20CFD, are presented in this report. The numerical designation in the identification label signifies the nominal film thickness in microns (μm). For comparisons of the material properties and performance attributes of the new co-extruded grades to a state-of-the-practice separator, a microporous polyethylene Tonen SETELA separator, grade E16MMS was employed. This mono-layer grade, which has been produced in Japan since the early 1990's, presently serves as the standard separator component in some lithium-ion cell designs. All separator samples were inspected for uniform appearance and thickness, and were stored in a low relative humidity (<2 percent) dryroom environment.

The procedure (Ref. 10) for determining the puncture strength of a separator sample utilized a blunt tip on the end of a digital force gauge which recorded the force at which the separator was punctured while slowly moving the tip into the material using a hand-wheel motored test stand. Specifically, an Imada DS2 force gauge (20 N or 2 kilograms-of-force (kgf) capacity) was employed and operated in conjunction with accompanying penetrating pins and a vertical hand wheel test stand.

For the characterization of key separator sample mechanical and rheological properties, including sample mechanical integrity at elevated temperatures for an assessment of safety performance, dynamic mechanical analysis (DMA) (Ref. 11) techniques were employed, utilizing a TA Instruments Q800 Dynamic Mechanical Analyzer, which is shown in Figure 2, located in a low-humidity dryroom. The Q800 DMA instrument can operate over a wide temperature range (-150 to 600 °C) and provides multiple modes of deformation including dual/single cantilever and 3-point bending, tension, compression, and shear. The sample clamps are individually calibrated for data accuracy and the elegant but simple design facilitates sample mounting.

In conjunction with pertinent, property-specific analytical methodologies, the DMA instrumental method is used to study a material's response to stress, temperature and frequency, among other variables. A sinusoidal, constant (step) or fixed-rate force is applied to a separator sample to cause a mechanical deformation and to measure the sample's response as a function of temperature or time. Specific experimental procedures for the measurement and analysis of a separator sample's (1) thermal shrinkage, (2) tensile strength, and (3) melt integrity characteristics can be found in Reference 10. The tabulated results presented in this report for these characteristics represent average values for at least five experimental sample trials.



Figure 2.—TA Instrument's Q800 DMA with accompanying computer.

Results and Discussion

Lithium-ion Cell Performance and Safety—Separator Effects

Although classified as an inactive cell component, the separator plays a critical role in obtaining practical and optimal cell-level performance and the inherent safety of the cell. In addition to initially possessing optimal properties for meeting the requirements for a specific application, the material properties must be uniform and stable over the desired application/mission life. With respect to cell and battery-level safety, the internal cell separator can complement safety control circuits possessing redundant safety features (e.g., CID, PTC, vent, etc.).

In order to achieve good performance, the separator should possess a uniform pore structure and exhibit desired dimensional stability (e.g., low shrinkage) and a high ionic conductivity when imbibed with electrolyte. The separator property of high ionic conductivity, which is a function of multiple material properties, has a pronounced effect upon such cell properties as capacity, rate performance, fast charge capability, overall cell resistance and cycle life. For safety concerns, the advantages of utilizing a thin separator must be weighed against the reduction in mechanical integrity, and the cell design should reflect such. External mechanical abuse (e.g., “nail” penetration or crush) or an internal short-circuit could result in an abnormal increase in cell temperature, which, as discussed below, could seriously compromise safety. If an undesirable cell overcharge condition occurs, dendritic lithium metal could form on the negative electrode surface, which could penetrate the separator and result in an internal short-circuit and an undesirable increase in internal cell temperature.

Thermal Properties and Separator Shutdown Performance

If a lithium-ion cell is accidentally overcharged or abused, heat can be generated that could seriously compromise cell and battery-level safety, which is especially critical for human-rated applications. Above a threshold temperature, a “self-heating” condition could occur due to exothermic reactions occurring internally within the cell (Ref. 12). Such reactions may include reactions between lithium and electrolyte and the thermal decomposition of internal cell components. If the internal heat generation is allowed to continue, a catastrophic “thermal runaway” condition could occur, which would be a serious safety concern for a manned application.

For battery safety with lithium-based cell chemistries, especially for manned applications, it is desirable for a state-of-the-art battery separator to possess an inherent ability to shut the battery down (i.e., terminate the flow of electric current) if overheating occurs. Near the melting temperature of the specific polymeric material, the pores collapse, and this event is accompanied by a significant increase in both the separator and overall cell impedances, resulting in a moderation of electrochemical activity and current flow. Optimization of the shutdown response and efficiency may be achievable by tailoring material properties and processing methods.

The separator material should also possess high-temperature *melt integrity*, and exhibit mechanical robustness above the shutdown temperature, as characterized by a high *rupture temperature*. After a separator shutdown occurrence, the cell temperature is likely to continue to increase. The separator must maintain mechanical integrity and high impedance at elevated temperatures in order to prevent the electrodes from making physical contact and creating the safety hazard of an internal short-circuit. Ideally, the mechanical integrity of the separator should be maintained for a long enough period of time for heat to be sufficiently dissipated and a thermal cool-down to occur. Dynamic mechanical analysis (DMA) provides a measure of a material’s melt integrity.

Mechanical Properties of ExxonMobil Polyolefin Battery Separator Materials

Puncture Strength

Puncture strength is the weight/force that must be applied to a needle or probe to force it completely through a separator. It is used to indicate the tendency of a cell separator to be resist penetration and internal short-circuiting that may be caused by the rough surface of an electrode during the battery assembly or by electrode surface changes that can occur during charge-discharge cycles. If particulate material from the electrodes penetrates the separator, an electrical short will occur, creating a safety hazard. The puncture strength should be at least 300 grams-of-force per mil of thickness (g/mil) for lithium-ion cells (Ref. 2).

Experimentally-measured relative values of puncture strength for the four co-extruded separator films and for the “baseline” Tonen, E16MMS, mono-layer grade material is presented in Figure 3, along with ExxonMobil literature values.

Figure 3 compares the average film experimental puncture strength values for at least five samples of each film grade, and the results are not normalized with respect to film thickness, so as to afford direct comparisons of the different films. In each material grade designation, the numerical portion refers to the material thickness in microns. The experimentally-measured numerical values are not absolute material specifications, as the measured values are only relative to the specific test conditions and methodology employed in our laboratory, and this is reflected by the differences shown between the experimental and the company-projected values in the figure. Comparing the Tonen E16MMS grade with the thicker co-extruded grades, the V20EHD and V25EKD grades show an enhanced safety feature with respect to puncture strength, which is coupled with a higher porosity (i.e., a higher power capability) for all four of the co-extruded grades.

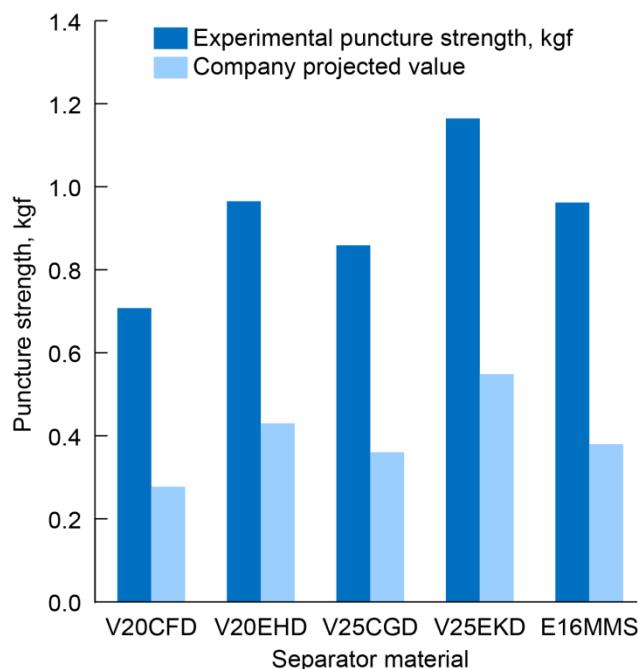


Figure 3.—Relative average puncture strength results for ExxonMobil/Tonen separator films.

Dynamic Mechanical Properties—Tensile Strength

The separator is typically wound with the electrodes under tension during cell fabrication. The winding machine combines the two electrodes and separator strip on a mandrel and winds the combination in a jellyroll fashion into a cell core. Cylindrical cells are wound on a round mandrel while prismatic cells utilize a flat paddle. The separator must not elongate significantly under the tension or change width. A tensile strength specification is sometimes given, but the key parameter is Young's modulus in the machine direction (MD). As Young's modulus is difficult to measure, the "2 percent offset yield" is a viable measure; less than "2 percent offset" at 1000 psi is acceptable for many winding machines (Ref. 2). This "offset yield strength" represents an approximation of the elastic limit of the material, and is expressed in terms of percent strain. It is the stress that corresponds to the point of intersection of a stress-strain graph and a line parallel to the straight line portion of the graph. Offset refers to the distance between the origin of the stress-strain diagram, and the point of intersection of the parallel line and the zero stress axis.

A separator should be strong enough to withstand mechanical handling during cell winding and assembly. It should be dimensionally stable and should not neck down (i.e., contract in width) during winding. A decrease in width will allow the electrodes to touch each other and create a short. Thus, the tensile property of the separator should be very strong in the machine direction (i.e., winding direction). The strength in the transverse direction is not as critical as that in the machine direction during the process of making spiral-wound batteries (Ref. 13). Flat-plate cells often utilize a wound electrode-separator sandwich, also, which is heated and pressed flat. For weaved or stacked cell components, which are held together by pressure, a tension-applying winding operation would not necessarily be employed in the cell fabrication.

While the separator is under tension and the percent strain is increased on the sample, the film experiences two types of deformations (1) elastic deformation, which is the distance that the film can be stretched and still return to its initial length, and (2) plastic deformation, in which the film is continually being stretched and becoming permanently deformed. The instrumental DMA analysis performed on the separator samples provides the following multiple indicators of separator strength while under tension:

- (1) Yield strength—Occurs at the transition from elastic to plastic deformation
- (2) Ultimate strength—Maximum stress that a material can undergo while under tension
- (3) Breaking strength—Stress on the material at the point of rupture

Representative graphical tensile strength data for a single experimental trial for the ExxonMobil separator films are shown in Figures 4 and 5 for the machine and transverse directions, respectively. Average results from the multiple trials are shown in Tables 2 and 3.

TABLE 2.—AVERAGE EXPERIMENTAL MACHINE DIRECTION TENSILE STRENGTH RESULTS FOR EXXONMOBIL SEPARATOR FILMS

Material	Displacement at break, μm	Strain at break, percent	Ultimate stress, MPa	Ultimate strain, percent	Stress at yield, MPa	Young's modulus, MPa
V20CFD	16532	222.6	32.91	205.0	18.3	153.2
V25CGD	19490	251.6	49.93	231.1	24.3	178.0
V20EHD	19030	240.2	50.96	205.04	26.14	210.3
V25EKD	17128	226.6	46.11	172.70	22.44	138.0
E16MMS	18190	235.3	57.28	216.2	16.30	156.6

TABLE 3.—AVERAGE EXPERIMENTAL TRANSVERSE DIRECTION TENSILE STRENGTH RESULTS FOR EXXONMOBIL SEPARATOR FILMS

Material	Displacement at break, μm	Strain at break, percent	Ultimate stress, MPa	Ultimate strain, percent	Stress at yield, MPa	Young's modulus, MPa
V20CFD	14152	171.5	54.48	130.5	36.26	305.4
V25CGD	18071	227.9	45.65	162.5	26.04	106.9
V20EHD	15538	191.5	69.60	166.1	45.75	176.5
V25EKD	15738	189.2	46.12	145.3	39.72	137.7
E16MMS	10570	127.2	67.21	92.63	42.31	301.8

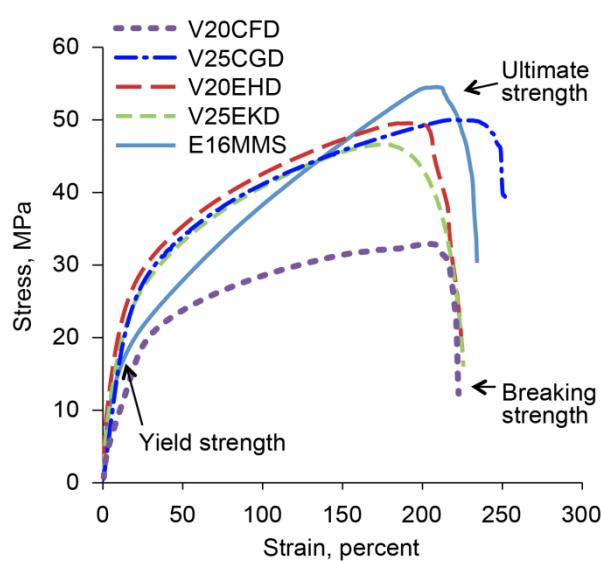


Figure 4.—Experimental machine direction tensile strength results for ExxonMobil separator films.

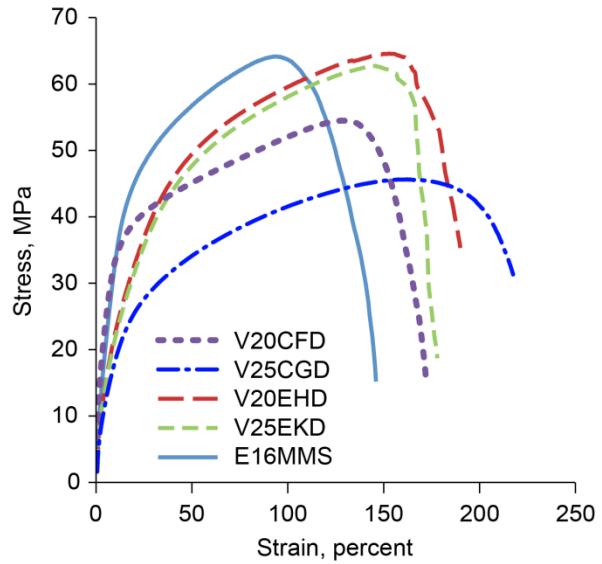


Figure 5.—Experimental transverse direction tensile strength results for ExxonMobil separator films.

Examining Figures 4 and 5, as the percent of strain applied to the film is increased, the amount of stress applied is also increased. When comparing the observed data for the machine direction to the transverse direction, the machine direction tends to require a higher percent strain in order for the separator to rupture. This is because the separator experiences a lower stress when transitioning from elastic to plastic deformation, therefore more strain can be applied before film rupture occurs. The point at which the graph turns from a relatively steep initial slope to a more gradual slope is where the transformation between elastic and plastic deformation occurs. In general, the tensile properties in both directions are of similar magnitude for all of these film grades, as they were fabricated by a wet-process, as described earlier, and do not exhibit anisotropy. Differences in tensile properties between the various grades can be attributed to differences in material composition and film processing. It can also be noted that as Young's modulus increases for the co-extruded grade materials in both the machine and transverse directions, there is a tendency for the ultimate stress to increase as well. In general, the percent strain at the breaking point for the co-extruded film grades was comparable to that for the E16MMS film in the machine direction, whereas significantly higher percent strain values were observed for the co-extruded films in the transverse direction.

Dynamic Mechanical Properties—Thermal Shrinkage

Lithium-ion batteries can be poisoned by water, and therefore materials going into a cell are typically dried at 80 °C under vacuum. Under these conditions the separator must not shrink significantly and certainly must not wrinkle. The requirement of <5 percent shrinkage after 60 min at 90 °C (in vacuum), is a reasonable generalization for comparing the shrinkage characteristics of separator films that may undergo drying protocols or be subjected to elevated temperatures.

The procedure to evaluate thermal shrinkage utilizing the DMA employed a very low constant 0.001N applied force that simulated holding the separator sample at a constant temperature with minimal applied tension. The temperature was rapidly ramped to 90 °C and then held isothermal for 1 hr. The displacement of the sample serves as an indicator of the shrinkage in the particular direction the sample was tested in. Representative graphical thermal shrinkage data for a single experimental trial for the ExxonMobil separator films are shown in Figures 6 and 7 for the machine and transverse directions, respectively. Average results from the multiple trials are shown in Tables 4 and 5.

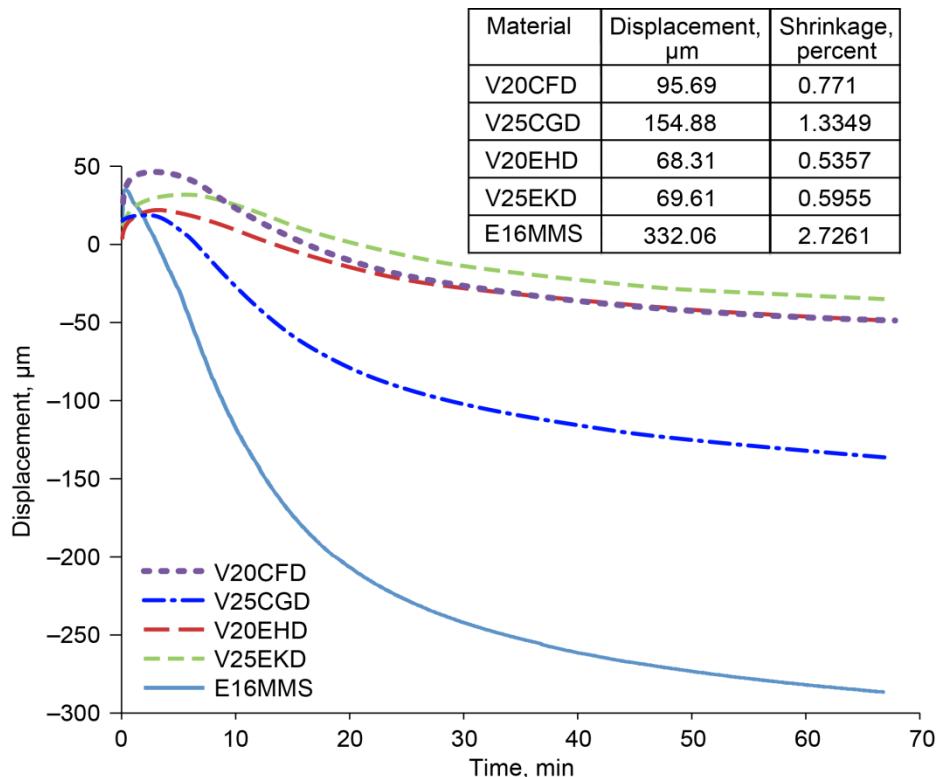


Figure 6.—Experimental machine direction thermal shrinkage results for ExxonMobil separator films.

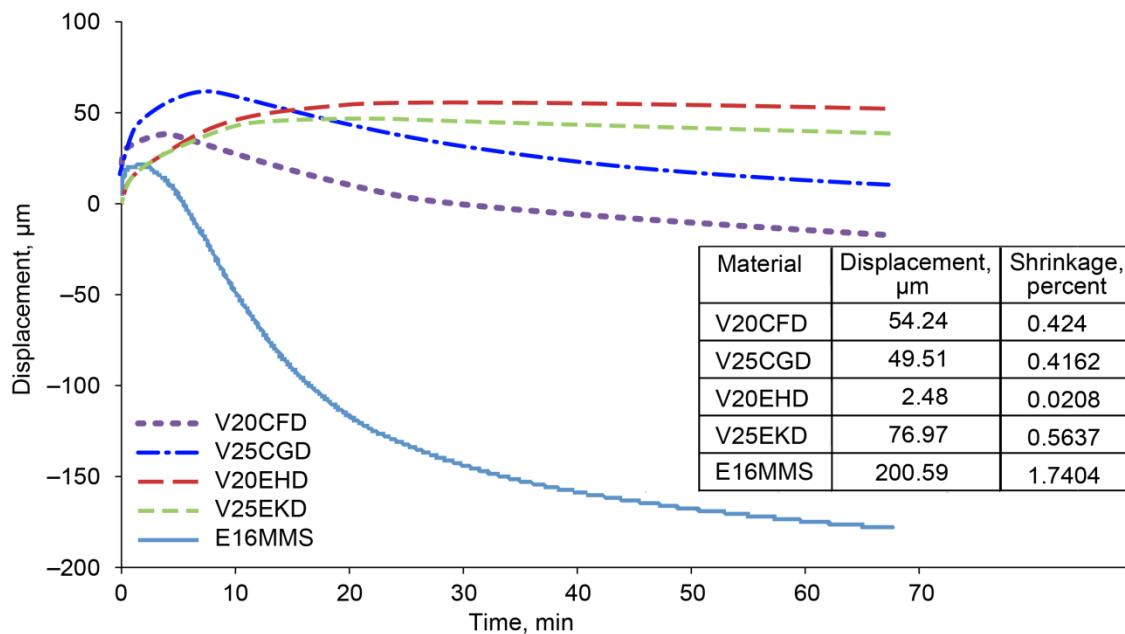


Figure 7.—Experimental transverse direction thermal shrinkage results for ExxonMobil separator films.

TABLE 4.—AVERAGE EXPERIMENTAL MACHINE DIRECTION THERMAL SHRINKAGE RESULTS FOR EXXONMOBIL SEPARATOR FILMS

Material	Average displacement, mm	Average shrinkage, percent
V20CFD	0.0947	0.8201
V25CGD	0.1574	1.3566
V20EHD	0.0679	0.5181
V25EKD	0.0805	0.5867
E16MMS	0.3237	2.7761

TABLE 5.—AVERAGE EXPERIMENTAL TRANSVERSE DIRECTION THERMAL SHRINKAGE RESULTS FOR EXXONMOBIL SEPARATOR FILMS

Material	Average displacement, mm	Average shrinkage, percent
V20CFD	0.0544	0.4254
V25CGD	0.0468	0.3945
V20EHD	0.0029	0.0244
V25EKD	0.0714	0.5432
E16MMS	0.1975	1.6986

Comparing the thermal shrinkage results in both machine and transverse directions, the average displacement and average shrinkage values for all of the film grades were higher in the machine direction. Even though these separator grades tend to shrink to a greater degree in the machine direction, none of the samples approached the maximum separator requirement limit of 5 percent shrinkage. As represented in Figure 6, the co-extruded grades exhibit significantly less thermal shrinkage than the E16MMS grade in the machine direction. Most of the co-extruded grade separators had relatively low thermal shrinkage results; all of them had less than 2 percent shrinkage in the machine direction and less than 1 percent in the transverse direction.

Dynamic Mechanical Properties—Melt Integrity

Melt integrity is a critical property that affects the mechanical and electrical properties of a battery. Separators with good mechanical integrity over a wide temperature range can provide a greater margin of safety for lithium-ion cells by preventing the electrodes from contacting one another. The temperature at which the separator loses physical integrity (viscosity becomes low enough to allow the electrodes to contact) can be identified by measuring the elongation of a separator film under load (~5 g/cm) as a function of temperature.

Utilizing thermal mechanical analysis (TMA) with a DMA, the separator film is held under a constant load/stress with a temperature ramp, and the degree of elongation or displacement is measured. The temperature at which the elongation increases dramatically is when the separator loses its mechanical integrity and, thus, its safety factor.

Typically, polyolefin separators show some shrinkage initially, and then start to elongate and, ultimately, break (rupture). This test utilizes a small separator sample (about 10 mm length (MD) and about 3 mm width (TD)), which is held in the film tension clamp. The sample is held under a small, constant 0.02 N force while the temperature is ramped at 5 °C per minute past the melting point of the material until the tension ruptures the film. Three parameters are reported from the procedure:

- (1) Shrinkage onset temperature
- (2) Deformation temperature
- (3) Rupture temperature

The locations of these temperature parameters on a typical melt integrity analysis curve plotting film displacement as a function of temperature are illustrated in Figure 8, in which curves for both a monolayer Tonen polyethylene material and a multi-layer (i.e., PP/PE/PP) Celgard separator material are shown for comparison. For enhanced internal cell safety, separators with a rupture temperature greater than 150 °C are desirable for lithium-ion cells.

In Figure 9, representative melt integrity data for a single experimental trial for the ExxonMobil separator films are presented graphically. Average results from multiple trials are summarized in Table 6. In these analyses, a chosen deformation temperature is representative of the transition from sample shrinkage to elongation. Melt integrity data was only compiled for displacement in the machine direction (MD); duplicate trials with the Tonen E16MMS film samples verified identical graphical results in both the MD and TD directions.

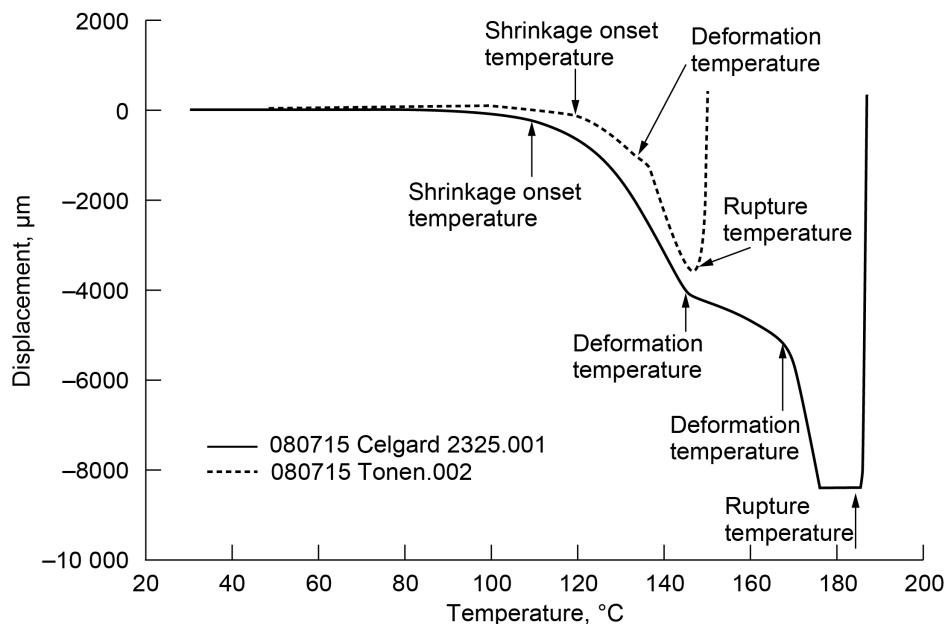


Figure 8.—Illustration of various temperature regimes for melt integrity analysis.

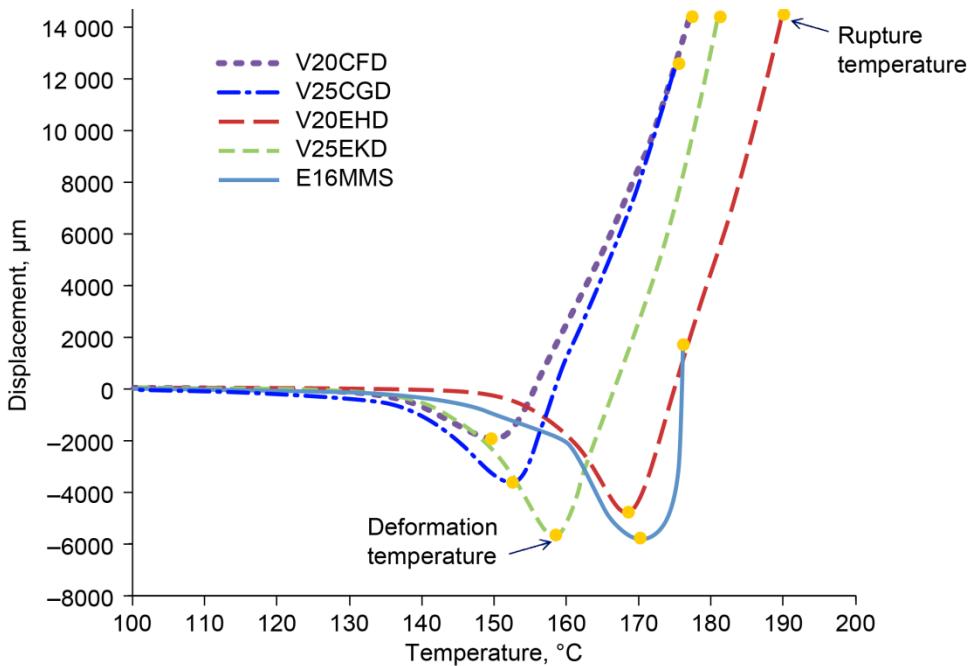


Figure 9.—Example of experimental melt integrity data for ExxonMobil separator films.

TABLE 6.—AVERAGE EXPERIMENTAL MELT INTEGRITY TEMPERATURE PARAMETERS FOR EXXONMOBIL SEPARATOR FILMS

Material	Shrinkage onset temperature, °C	Deformation temperature, °C	Rupture temperature, °C
V20CFD	125.38	150.15	178.38
V25CGD	129.34	153.8	181.4
V20EHD	157.3	167.7	191.1
V25EKD	142.68	162.92	183.63
E16MMS	121.35	160.3	173.06

As illustrated in Figure 9, the graphical representation shows a general trend for the co-extruded grades—for a grade with a higher observed deformation temperature, a higher rupture temperature is also observed. The V25EKD and the V20EHD materials exhibiting the highest rupture temperatures of the four co-extruded grades. As the films are being heated, between their shrinkage onset temperatures and their defined deformation temperatures the polyolefin fibril compositions are undergoing melting, which is accompanied by a decrease in the film porosity. If this occurred in a lithium-ion cell, the separator would be undergoing the “shutdown” phenomena, accompanied by a significant increase in separator and overall cell impedances, as described earlier. Following shutdown, the melt integrity data shows that the co-extruded grades, with their higher rupture temperatures relative to the E16MMS grade, would afford a higher degree of separator mechanical integrity and electrode isolation for a longer period of time as the temperature continued to rise to the point of actual rupture (i.e., total separator meltdown). Also, the lower slope of the displacement versus temperature data exhibited for the co-extruded grades after their deformation temperatures are reached reflects a more gradual increase in strain upon and meltdown of the separator compared to the mono-layer grade material.

Conclusions

The laboratory assessment results for the puncture strength and dynamic mechanical properties for four grades of novel ExxonMobil co-extruded polyolefin battery separators suggest that these materials may afford an enhanced level of internal safety-related performance and reliability for lithium-ion cell chemistries relative to some current state-of-the-practice cell separator component materials. The improved meltdown properties of these materials extend the integrity of the electrode-separating barrier for a longer time during a thermal event, allowing the cell additional time to dissipate heat and avoiding the occurrence of a more catastrophic event. Improved permeability attributes of these materials may also afford enhanced cell-level energy and power capabilities.

As ExxonMobil and other companies advance their separator material development and manufacturing capabilities to address forthcoming electric vehicle market opportunities, it is of interest to NASA to leverage such technology advancements in order to address its advanced energy storage and battery technology needs for future aerospace missions, especially when enhanced safety and high reliability are highly desired for manned missions. For advanced high-energy lithium-ion cell designs, such as those addressed by the NASA ETDP Energy Storage Project, enhanced cell-level safety performance, which could be afforded by a slightly thicker and higher temperature-tolerant separator component as compared to “baseline” materials, could overshadow a rather minimal projected negative impact on cell specific energy due to an increased component mass (i.e., separator and its imbibed electrolyte) and volume. Depending upon mission power and rate requirements, the enhanced permeability characteristics of the safety-enhanced ExxonMobil co-extruded materials could offset cell specific energy differences even further.

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14. ABSTRACT As NASA prepares for its next era of manned spaceflight missions, advanced energy storage technologies are being developed and evaluated to address future mission needs and technical requirements and to provide new mission-enabling technologies. Cell-level components for advanced lithium-ion batteries possessing higher energy, more reliable performance and enhanced, inherent safety characteristics are actively under development within the NASA infrastructure. A key component for safe and reliable cell performance is the cell separator, which separates the two energetic electrodes and functions to prevent the occurrence of an internal short-circuit while enabling ionic transport. Recently, a new generation of co-extruded separator films has been developed by ExxonMobil Chemical and introduced into their battery separator product portfolio. Several grades of this new separator material have been evaluated with respect to dynamic mechanical properties and safety-related performance attributes. This paper presents the results of these evaluations in comparison to a current state-of-the-practice separator material. The results are discussed with respect to potential opportunities to enhance the inherent safety characteristics and reliability of future, advanced lithium-ion cell chemistries.				
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